

The NASA “PERS” Program: Solid Polymer Electrolyte Development for Advanced Lithium-Based Batteries

Richard S. Baldwin
Glenn Research Center, Cleveland, Ohio

William R. Bennett
QSS Group, Inc., Cleveland, Ohio

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI program provides access to the NASA Aeronautics and Space Database and its public interface, the NASA Technical Reports Server, thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services also include creating custom thesauri, building customized databases, organizing and publishing research results.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA STI Help Desk at 301-621-0134
- Telephone the NASA STI Help Desk at 301-621-0390
- Write to:
NASA Center for AeroSpace Information (CASI)
7115 Standard Drive
Hanover, MD 21076-1320



The NASA “PERS” Program: Solid Polymer Electrolyte Development for Advanced Lithium-Based Batteries

Richard S. Baldwin
Glenn Research Center, Cleveland, Ohio

William R. Bennett
QSS Group, Inc., Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

Level of Review: This material has been technically reviewed by technical management.

Available from

NASA Center for Aerospace Information
7115 Standard Drive
Hanover, MD 21076-1320

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161

Available electronically at <http://gltrs.grc.nasa.gov>

The NASA “PERS” Program: Solid Polymer Electrolyte Development for Advanced Lithium-Based Batteries

Richard S. Baldwin
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

William R. Bennett
QSS Group, Inc.
Cleveland, Ohio 44135

Abstract

In fiscal year 2000, The National Aeronautics and Space Administration (NASA) and the Air Force Research Laboratory (AFRL) established a collaborative effort to support the development of polymer-based, lithium-based cell chemistries and battery technologies to address the next generation of aerospace applications and mission needs. The ultimate objective of this development program, which was referred to as the Polymer Energy Rechargeable System (PERS), was to establish a world-class technology capability and U.S. leadership in polymer-based battery technology for aerospace applications. Programmatically, the PERS initiative exploited both interagency collaborations to address common technology and engineering issues and the active participation of academia and private industry. The initial program phases focused on R&D activities to address the critical technical issues and challenges at the cell level. Out of a total of 38 proposals received in response to a NASA Research Announcement (NRA) solicitation, 18 proposals (13 contracts and 5 grants) were selected for initial award to address these technical challenges. Brief summaries of technical approaches, results and accomplishments of the PERS Program development efforts are presented.

With Agency support provided through FY 2004, the PERS Program efforts were concluded in 2005, as internal reorganizations and funding cuts resulted in shifting programmatic priorities within NASA. Technically, the PERS Program participants explored, to various degrees over the lifetime of the formal program, a variety of conceptual approaches for developing and demonstrating performance of a viable advanced solid polymer electrolyte possessing the desired attributes, as well as several participants addressing all components of an integrated cell configuration. Programmatically, the NASA PERS Program was very successful, even though the very challenging technical goals for achieving a viable solid polymer electrolyte material or the overall envisioned long-term, program objectives were not met due to funding reductions. The NASA PERS Program provided research opportunities and generated and disseminated a wealth of new scientific knowledge and technical competencies within the polymer electrolyte area.

Background

Rechargeable lithium-based battery technologies offer significant performance advantages and cost benefits for a variety of future aerospace, as well as terrestrial missions. Major projected advantages over more conventional battery technologies include reduced mass and volume of the energy storage system, enhanced system reliability and flexibility and lower power system life-cycle costs. NASA and aerospace mission planners recognize the viability of utilizing lithium-based batteries in many future aerospace applications, such as planetary landers, planetary rovers, planetary orbiters, Earth-orbiting spacecraft for both geosynchronous

(GEO) and low-Earth-orbit (LEO) missions, reusable launch vehicles (RLVs) and astronaut equipment. Some lithium-based chemistries have already been space-qualified and serve as the electrochemical power subsystem for selected aerospace missions. In addition, the feasibility of replacing the hydraulic Auxiliary Propulsion Unit (APU) of the existing Space Transportation System with an electrically controlled system that will utilize lithium-based batteries is being assessed. The U.S. Air Force also envisions the use of lithium-based batteries in various applications, such as unmanned aerial vehicles, military aircraft and Earth-orbiting spacecraft. Other governmental agencies, including the Department of Energy (DOE) and the Department of Defense (DoD), also envision the future use of lithium-based battery technologies to enhance or to enable their specific mission needs.

Cell and battery requirements for future NASA and Air Force missions span a wide range and are determined by specific mission needs. For example, LEO spacecraft and planetary orbiters require batteries that can provide greater than 30,000 cycles at up to 30 to 40% depth-of-discharge (DOD). GEO applications will require a long calendar life in excess of twenty years. Planetary missions such as rovers and landers require batteries that are capable of operating at low temperatures following the long stand time associated with travel to reach the planet. Some aircraft and RLV applications require high voltage and high capacity batteries with the capability of performing over a very wide temperature range. Commercially available lithium-based cells fail to meet many of the aerospace mission requirements, and the safety of high capacity cells and batteries is also a serious concern for aerospace applications. State-of-the-art lithium-ion cells need significant performance improvements in several areas in order to address aerospace mission needs.

In order to address the advancement of the state-of-the-art of lithium-ion cells and batteries to meet NASA and Air Force mission needs, a collaborative DoD/NASA program effort was initiated in 1997. The program utilized a technical approach focusing on cell design optimization and the development of advanced electrode materials and liquid electrolytes to achieve improved low-temperature performance and cycle life. The program objectives included (1) the development of high performance lithium-ion cells and batteries along with (2) the development of control electronics for "smart" battery management, (3) the establishment of production sources and (4) the demonstration of technology readiness for various mission applications. The total estimated value of the program from both USAF and NASA funding was ~\$23M.

To address the electrochemical energy storage needs for the next generation of aerospace applications, advanced lithium-based cell chemistries that are coupled with solid-state and/or polymer-based component concepts are envisioned to be mission-enhancing and mission-enabling technologies. For such future applications, the energy storage subsystem must have minimal mass, while meeting the power requirements of the spacecraft or of the mission-specific device. The current view was that no single cell chemistry will optimally meet all aerospace mission needs. The successful development of such advance technologies would also have significant impact on commercial and terrestrial applications.

“Pre-PERS Program” Advanced Polymer Battery Development

Up to the year 2000 timeframe, non-NASA governmental support of polymer-based battery technology development had included (1) DoD (USAF/Army/Naval Research Laboratory) contributions totaling ~\$4.8M from FY 1997 to FY 2000, (2) DOE and the United States Advanced Battery Consortium expenditures of ~\$24.5 M over the previous 5 years to develop polymer battery technology, primarily for the electric vehicle market and (3) the DOE Exploration Technology Research (ETR) Program, in collaboration with industry and academia, investment of ~\$1.5M from FY 1998 to FY 2000. In addition, the commercial battery industry was developing a small version of the technology for portable electronics and communications.

NASA funding for polymer-based battery technology development had been at a low level prior to fiscal year 2000. It included ~\$300K for grants and contracts awarded in FY 1999 and, over the previous several years, several Small Business Innovative Research (SBIR) proposals were awarded in the technical area. The available FY 1999 funding allowed the initiation of several short-term, fundamental research investigations that supported R&D objectives. The focus of these investigations was to evaluate some diverse solid polymer electrolyte chemistries and conceptual approaches and to perform a preliminary assessment of the "practical" technical feasibility of utilizing these exploratory materials for "liquid-free" lithium-ion transport in lithium-based rechargeable cells. The results of these investigations were made available in the open literature, as appropriate. Also, from FY 1996 to FY 1998, NASA GRC personnel served as contract managers for a DARPA-funded Technology Readiness Program for the development of a polymer battery, which was a combined \$6M effort, with the Government contribution at \$1.8M.

PERS Programmatic Approach

With the availability of substantial NASA funding occurring in fiscal year 2000, NASA and the Air Force Research Laboratory expanded collaborative efforts to support the development of polymer-based, lithium-based cell chemistries and battery technologies in order to address future aerospace mission needs with the formal Polymer Energy Rechargeable System (PERS) Program initiative. The ultimate objective of this development program was to establish a world-class technology capability and U.S. leadership in polymer-based battery technology for aerospace applications. Once fully developed, this technology was envisioned to be superior to other conventional battery technologies.

Advanced lithium-based cell chemistries coupled with polymer-based component concepts offer numerous advantages over battery systems employing a liquid electrolyte. An all-solid cell design, which contains no free liquid, offers inherent safety advantages, e.g., no internal pressure buildup, and affords a reduction in system complexity. As the same high unit cell voltages that are exhibited by lithium-based liquid electrolyte cells are achievable, higher specific energies and energy densities, coupled with lower self-discharge rates, are also projected improvements for solid electrolyte cell concepts. A flexible shape factor in cell design will enable integration of the energy storage system with structural or other subsystem entities. Also, the exploitation of polymer film-based manufacturing technologies is projected to result in significant production cost reductions.

The PERS program approach was to address both near-term and far-term R&D issues and technical challenges that are critical for successful development of the polymer-based battery technology. The initial phases of the program focused on the development of the critical cell components in order to achieve necessary levels of performance. This included the development of solid polymer electrolytes, the development of anode and cathode materials that are compatible with the electrolyte and the achievement of desired electrode/electrolyte interfacial properties. The programmatic approach taken for this critical component development was to support as many novel R&D concepts and technical approaches as were viable with existing program funding. Some examples of far-term issues and needs were component/cell scale-up, cell/battery designs to address specific applications, complex charge control requirements, subsystem integration issues, thin-film fabrication technologies and the establishment of appropriate manufacturing processes.

The primary near-term PERS program focus was to support the development of solid polymer electrolytes that exhibit the technical performance necessary for achieving a viable cell/battery. The electrolyte performance requirements (as summarized in Table 2), include (1) an ionic conductivity of $\sim 10^{-3}$ S/cm or higher in the desired operational temperature range (e.g., -40 to 65 °C), (2) a lithium-ion transport number approaching unity, (3) low interfacial

impedance, (4) chemical compatibility with electrode materials, (5) a large window of electrochemical stability, (6) low electronic conductivity, (7) good dimensional and thermal stability and (8) mechanical properties that allow scale-up of the manufacturing process. Electrolyte chemistries and concepts under consideration included (1) polymer electrolytes based on "solvent-free" binary salt complexes, (2) cation-conducting polyelectrolytes, (3) polymer-ceramic composites, (4) inorganic-organic hybrids and (5) hybrid/gelled systems.

Envisioned as a multi-year effort with initial programmatic emphasis on the development of critical cell components and technologies, the PERS program was structured as a collaborative and cooperative national interagency technology development initiative. This approach was to not only leverage existing government-sponsored related R&D programs, but to ensure the effective utilization of government funding, skills and resources to address technology and engineering issues of mutual interest. In early 2000, an Interagency PERS Program Working Group meeting was held to aid in creating the collaborative interagency relationships that were then being defined and pursued. This forum was invaluable in assessing current R&D programs, identifying key technical issues, avoiding duplications of technical efforts and discussing areas of mutual interest for collaboration and knowledge leveraging. Representatives from the DoD (AF/Navy/Army), DOE, and CIA attended the workshop.

The realization of the formal PERS Program in FY 2000 was the result of a Congressional augmentation of ~\$4.6M to the NASA budget for increased R&D on the polymer battery technology. The NASA Glenn Research Center (GRC) was tasked to lead the effort in collaboration with the U.S. Air Force (USAF) Research Laboratory, Wright-Patterson AFB, Ohio. Polymer-based battery R&D tasks initiated with this augmentation included (1) AFRL in-house polymer electrolyte development, (2) Jet Propulsion Laboratory (JPL) in-house polymer electrolyte development, (3) GRC in-house polymer electrolyte development and (4) the establishment of a lithium-based battery component screening facility and infrastructure at GRC to support the overall program development efforts. Also, funding was provided to the AFRL to support a Dual-Use Science & Technology (DUS&T) contract with Eagle-Picher Technologies, LLC and the University of Dayton Research Institute for mission-specific polymer electrolyte development.

As previously mentioned, the initial phases of the PERS program were to focus on addressing the key technology issues and challenges that exist at the cell and component level. In addition to exploiting interagency collaborations, this was to be accomplished programmatically by (1) the effective utilization of internal NASA and AFRL facilities, resources and expertise in electrochemistry, battery technology, polymer chemistry and materials science and (2) the collaborative and interactive involvement of both academia and private industry. [Richard S. Baldwin, et al., Polymer Energy Rechargeable System (PERS) Development Program, 39th Power sources Conference, Cherry Hill, NJ (2000)]

The active involvement of the academic and business communities in the PERS program fundamental R&D activities was addressed in FY 2001 with continued funding augmentation via the mechanism of a NASA Research Announcement (NRA). This solicitation for research proposals for open competition focused on the development of the polymer electrolyte and other critical cell components of interest to meet envisioned cell-level performance requirements. All polymer-based cell chemistries and concepts were considered, and successful offerors were expected to be able to substantiate incremental progress in demonstrating technical feasibility by meeting short-term milestones within their PERS-supported programs. One-year to three-year efforts were solicited, and contract/grant renewal on an annual basis was contingent upon acceptable technical progress and continued funding availability. Out of a total of 38 proposals received in response to the NRA solicitation, 18 proposals (13 contracts and 5 grants) were selected for initial award. A register of the selected external efforts is presented in Table 1. Established R&D efforts at the AFRL, JPL and internally at GRC also continued with FY 2001

funding. As a result of reductions in program funding during the subsequent fiscal years, it became necessary to cancel R&D efforts that were felt to be less technically viable.

Table 1.—NASA PERS Program initially selected technical efforts.

PERS PROGRAM SELECTED CONTRACTORS AND GRANTEES	
Covalent Associates	Advanced Lithium Polymer Electrolyte for Li-Ion Batteries
Eagle-Picher Technologies, LLC - Joplin, MO	Novel Host Materials for Ceramic Electrolytes
EIC	Lithium Based Polymer Electrolyte Battery
Indiana University	Nanostructured Single-Ion SPE for Lithium Batteries
InvenTek	Development of Solvent-Free High Performance Li-Polymer
Lawrence Berkeley National Laboratory (LBNL)	Advanced Polyelectrolyte Separators for Rechargeable Lithium Batteries
LITHCHEM International	New Stable, More Conductive Solid Polymer Electrolyte
Lithium Power Technologies	Polymer Electrolytes for Solid-State Lithium Batteries
Lockheed Martin / Comsat	Lithium Based Polymer Battery Development of Solid Polymer Electrolyte and Manganese Spinel Cathode
Max Power / Temple University	An Integrated Approach to Develop a High Energy Density Long Cycle Life Lithium Based Polymer Battery
Naval Air Warfare Center Weapons Division (NAWCWD)	New Solid Polymer Membranes for Rechargeable Lithium Batteries
National Center for Microgravity Research	Thermal Modeling of Lithium Based SPE Battery in Microgravity Applications
Northwestern University	Development of Highly Conductive Polyelectrolytes for Lithium Batteries
Physical Sciences, Inc.	High Performance Li-Ion Polymer Electrolyte with Pendant Anion Receptors
Texas Engineering Experimental Station (TAMU)	Advanced Li-Ion Polymer Batteries for Aerospace Applications
University of Minnesota	New Polymer Electrolyte Cell Systems
University of Utah	A Joint Simulation and Experimental Study of Nanocomposite Polymer Electrolytes
Yardney Technical Products	Development of a Lithium-Based Polymer Energy Rechargeable System for Future Space Applications
PERS PROGRAM GOVERNMENTAL PARTICIPANTS	
NASA Glenn Research Center (GRC) / University of Akron	Novel Molecular Architectures for Improved Solid Polymer Electrolytes for Lithium Polymer Batteries
Air Force Research Laboratory (AFRL) - WPAFB	Ionically-Conducting Channel Polymer Electrolytes
Jet Propulsion Laboratory (JPL)	Solid Polymer Electrolyte Development

With Agency support provided through FY 2004, the formal PERS Program was concluded in 2005 due to internal reorganizations, funding cuts and shifting programmatic priorities within NASA. During FY 2005, the program efforts that remained were transitioned into the Advanced Battery Technology Development Program at NASA GRC.

An important element of the PERS Program infrastructure was the overall program technical support afforded by the state-of-the-art component screening facility established at GRC. In-house capabilities include the electrochemical screening and performance evaluation of solid polymer electrolyte (SPE) and electrode cell component materials, full-cell charge-discharge cycling evaluations as a function of temperature and the fabrication of cell components and

various test cell configurations under inert and/or ultra-low moisture environments. Moisture-sensitive material handling and component fabrication is performed within a 600 ft² dry room, as well as in dedicated argon-atmosphere gloveboxes. Goals for the critical parameters of SPE materials are summarized in Table 2. Experimental procedures to provide “standardized” measurements of the critical electrolyte properties were developed in-house and documented [W.R. Bennett & M.A. Manzo, *Preliminary Evaluations of Polymer-based Lithium Battery Electrolytes under Development for the Polymer Energy Rechargeable Systems Program*, 1st International Energy Conversion Engineering Conference (IECEC), Portsmouth, VA (2003)].

Table 2.—Goals for the critical parameters of SPE materials.

CRITICAL SPE MATERIAL PARAMETERS	
•	High ionic conductivity ($\sim 10^{-3}$ S/cm)
•	Low Electronic Conductivity ($< 10^{-12}$ S/cm)
•	Electrochemical Stability Window 0 to > 4 V
•	Favorable Li ⁺ transport properties
•	Li ⁺ transference number approaching 1
•	High salt diffusion coefficient
•	Favorable Interfacial Properties
•	Low interfacial impedance
•	Stable transport properties
•	Thermal stability
•	Mechanical toughness

Electrochemical screening and performance evaluation capabilities are complemented by in-house laboratory capabilities for the analysis and characterization of polymeric and inorganic materials via state-of-the-art thermal, imaging and spectroscopic methodologies. An Imaging & Material Analysis Laboratory is equipped with a scanning electron microscope energy dispersive spectrometer (SEM-EDS), a scanning probe microscope (SPM), an inductively-coupled plasma optical emission spectrometer (ICP-OES), a gas chromatograph-mass spectrometer, a stereomicroscope and a BET surface area analyzer. A Thermal & Material Analysis Laboratory is equipped with a differential scanning calorimeter (DSC), a thermogravimetric analyzer (TGA), a Raman spectrometer, a Fourier Transform infrared spectrometer (FTIR) and a particle size analyzer. Also, a dynamic mechanical analyzer (DMA) is available in the dry room for material rheological measurements. An accelerating rate calorimeter (ARC) is available for material compatibility and safety evaluations.

Synopses of Selected Technical Approaches and Accomplishments

In this section, brief summaries of technical approaches, results and accomplishments are presented for those contractual, grant and governmental efforts which demonstrated the most potential during the PERS Program, with respect to meeting the program’s technical objectives. Specific and/or detailed information and data that could be considered as proprietary or contractor-sensitive in nature will not be discussed herewith. If desired, more in-depth information can be obtained from the cited references and/or by contacting the principal investigators directly.

Lawrence Berkeley National Laboratory (LBNL)—John Kerr

The approach taken by LBNL was to develop single-ion conductor (SIC) solid polymer electrolytes (polyelectrolytes or ionomers) with enhanced lithium-ion conductivity based upon comb-branch polymer networks. A novel iterative approach was utilized, which was based upon

modeling and evaluation of binary salt-polymer systems and baseline materials to guide SIC material modification and optimization. The overall effort generated a wealth of new fundamental scientific knowledge, which has been disseminated via many technical publications and presentations, but has not yet achieved its technological goals to provide practical materials for lithium batteries.

The initial phase of the overall effort focused on the synthesis, characterization and electrochemical evaluation of lithium polyelectrolytes containing sulfonate-based anionic functional groups fixed to the sidechains of a comb-branch network polymer, as represented in figure 1. Optimized polymeric architectures, as well as synthetic routes, were elucidated for obtaining optimum ionic conductivity in the bulk electrolyte, and structure-conductivity correlations were identified. The abolishment of concentration polarization was also demonstrated with the utilization of SIC electrolytes, however, high interfacial impedances were observed for both solid and plasticized gel electrolytes [*Macromolecules*, **39**, 362 (2006)]. The expected benefits to ionic conductivity by employing fluorinated anionic moieties was also demonstrated [*Abstracts of Papers of the American Chemical Society*, **228**, U352-U352 (2004)].

With guidance derived from the initial phase of the effort, the second phase was to synthesize and characterize fluorinated polyelectrolytes containing more complex imide- and methide-based anionic moieties. Due to unforeseen difficulties related to precursor availability and synthesis, the program objectives related to the study of these specific materials were not fully realized, however, they are still being addressed for NASA, as initial work has demonstrated the advantage of employing imide anions in the SIC materials. To address the planned objectives of fully exploring the electrochemical and mechanical aspects of SICs in spite of these difficulties, efforts were refocused on the development of a new LiBAMB Network SIC system, which employed an anion based on borate esters (BAMB). SIC material optimization for bulk conductivity and mechanical properties, as well as initial electrochemical cell performance testing, was successfully completed with the LiBAMB anion-containing materials [*Macromolecules*, **39**, 362 (2006)].

In summary, the LBNL effort demonstrated and elucidated many advantages of utilizing SIC electrolytes in future lithium battery configurations, as well as identifying key technical barriers which must be overcome for the practical utilization of such. Polymer architectures optimized for bulk ionic transport properties can be synthesized, and these properties should be satisfactory under all desired operational temperature conditions when plasticized with solvent. The interfacial behavior of the SIC electrolytes is presently impractical, and future research in this area is needed to be able to embody these novel materials in future, practical lithium cell chemistries.

In addition to the focused efforts for lithium-based batteries, the synthesis work performed at LBNL for the NASA PERS Program was leveraged by the DOE Fuel Cell Program, as the specific polymer chemistries were found to be viable for addressing PEM fuel cell goals of achieving high proton conductivity with low humidity at elevated temperatures.

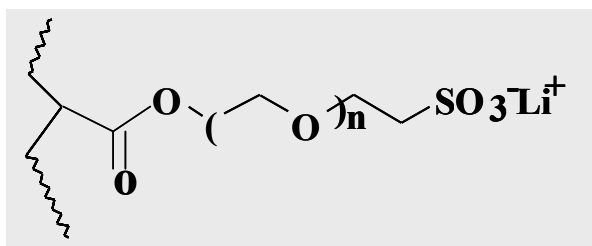


Figure 1.—Lithium-ion conducting comb-branch polymer sidechain.

NASA Glenn Research Center (GRC)—Mary Ann Meador

Research efforts within the NASA GRC Materials Division focused on exploring the synthesis and characterization of solid polymeric electrolytes with novel molecular architectures and/or ionic transport mechanisms, which were perceived to improve bulk ionic conductivity over a wider temperature range of practical interest, physical stability and processability. Approaches, which included self-assembling systems, liquid crystals and organic-ceramic hybrids, focused on introducing free volume and short-range order into the polymeric systems.

Primary in-house efforts focused on self-assembling rod-coil polymers in which polyimide rods form mechanical support for conducting polyethylene oxide (PEO) coils. The rods and coils phase separate, resulting in ion-conducting nanoscale channels. Statistically-designed experiments were employed to identify optimum compositions for the rod-coil architecture [Chemistry of Materials, **15**, 3018 (2003)].

Electrochemical screening evaluations of the rod-coil materials containing the binary lithium bis(trifluorosulfonyl imide) (LiTFSI) salt indicated that the best achievable room temperature (25 °C) bulk ionic conductivity has been $\sim 3 \times 10^{-5}$ S/cm. As shown in figure 2, bulk conductivity data for rod-coil SPEs compare favorably with data for high molecular weight PEO at temperatures below 40 °C, although practical cell performance is only viable at higher temperatures. In contrast to PEO materials, the rod-coil SPEs have excellent mechanical properties and remain solid at temperatures in excess of 200 °C. Electrochemical stability measurements showed an onset of decomposition at ~ 4 volts versus Li/Li^+ , similar to low-molecular weight PEO. Transport properties were experimentally found to be similar to PEO electrolytes [W.R. Bennett & R.S. Baldwin, *Assessment of Lithium-based Battery Electrolytes Developed under the NASA PERS Program*, 4th International Energy Conversion Engineering Conference (IECEC), San Diego, CA (2006)]. These rod-coil polymer materials are still under investigation, with emphasis on structural optimization, the incorporation of fixed anionic sites to produce ionomers and the incorporation of low-volatility supporting ionic liquid electrolytes imbedded within the polymer matrix.

A second approach that was explored focused on a series of Organically Modified Ceramic (ORMOCER) materials containing an organic portion that facilitates the transport of lithium ions through the polymer film and a cross-linked silica network to provide dimensional stability (see fig. 3). These materials exhibited good mechanical and electrochemical stability and

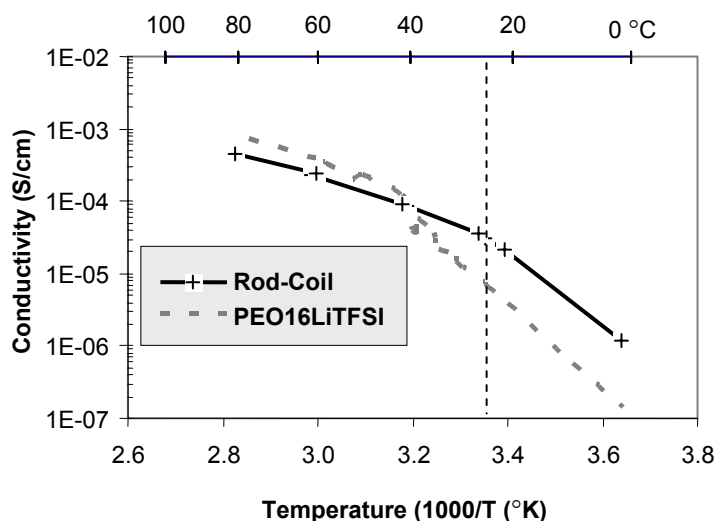


Figure 2.—Comparison of bulk conductivity data for rod-coil and PEO polymer electrolytes.

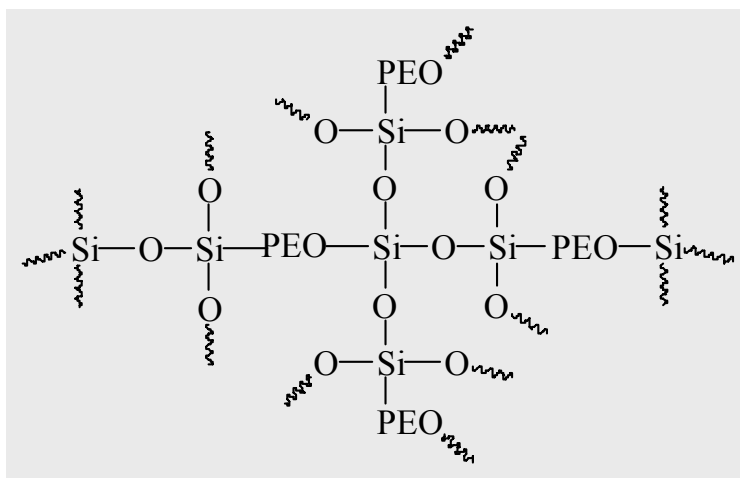


Figure 3.—Organically Modified Ceramic (ORMOCER) architecture.

temperature-dependent ionic conductivities similar in magnitude to the rod-coil materials. Performance-enhancing modifications to this class of materials were also investigated via cross-linking other inorganic oxides into the framework and via functionalizing the polymer backbone with a fixed anion to increase the lithium-ion transference number.

Several additional approaches to achieving viable molecular architectures were also explored, but with limited success, to-date. One approach involved the synthesis of discotic liquid crystalline polymers, which should stack to form highly-ordered ion-conducting channels. This architecture embodies disk-shaped molecules with three to six PEO sidechains attached. Also, an approach involving the use of melamine as a crosslink to provide highly-branched ethylene oxide polymers was investigated.

During the initial phase of the PERS Program, the NASA GRC in-house efforts were supported by two grants awarded to researchers at the University of Akron to explore their novel approaches. One approach was to synthesize a PEO-based homopolyrotaxane, where the PEO was threaded through a macrocrown ether. This was proposed to separate the PEO strands to increase the free volume in the polymer and improve dimensional stability. Materials that were able to be synthesized were liquid-like in nature and possessed very low ionic conductivities. A second approach was to employ diblock and graft copolymers with a polystyrene backbone containing oligomeric PEO sidechains.

Texas Engineering Experimental Station (TEES)—A. John Appleby

Located at Texas A&M University, the TEES effort focused on the development and evaluation of a complete lithium-ion polymer cell containing an advanced composite solid polymer (CSP) electrolyte containing Li^+ -conducting glasses and composite anode and cathode structures. Although the overall effort has not achieved, to-date, its technological goal of demonstrating a viable solid-state cell incorporating the proposed advanced components, a wealth of fundamental scientific knowledge was generated and disseminated via 16 conference presentations, several invention disclosures and over three dozen publications in the public domain.

The objective of the first task area was to develop nano-composite anodes with nanoparticles of selected materials of high reversible and low irreversible capacity uniformly dispersed in an elastic mixed-conductor optimized for effective cyclability. Over the course of the effort, many composition and synthesis variables were elegantly explored, correlated with electrochemical performance and optimized. Novel experimental methodologies were also

developed for studying mixed electronic and ionic conducting electrode substrates. The optimal choice for cell testing was found to be a (nano-Si-graphite-polyethylene oxide (PEO)-Li⁺-conducting ceramic) nano-composite anode structure [Wang, et. al., *J. Power Sources*, **125**, 206 (2004)].

The objective of the solid polymer electrolyte development task was to develop and characterize novel glass/ceramic particle or fiber-polymer composite electrolytes having high bulk ionic conductivity, high Li⁺ transference number and high interfacial stability. Various Li⁺-conducting glass particles and La_{0.55}Li_{0.35}TiO₃ fiber were synthesized and evaluated. After exhaustive evaluations and the identification of performance-limiting technical barriers, a highly-conducting ceramic fiber mat material was developed and was to be incorporated in the composite PEO-based solid electrolyte. Problems with optimized material reproducibility and fiber synthesis issues prevented cell testing, to-date, with the composite electrode materials [*J. Electrochemical Society*, **152**, A205 (2005)].

The advanced composite cathode development task for the TEES effort was performed under a subcontract at the University of Texas at Austin, under the direction of A. Manthiram, and many of his publications related to the effort can be found in the literature. Focus was on cathode systems which would combine high capacity with good cyclability, rate capability and long-term stability. During the multi-year effort, many novel cathode materials were synthesized, characterized and electrochemically evaluated in order to elucidate structure-property-performance relationships to guide development of optimal material for compatibility with a solid polymer electrolyte. Various nanostructured high-capacity oxide cathode materials were developed, including vanadium oxides, manganese-based spinel oxides and many stoichiometric variations of layered oxide materials, such as LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂. Several promising high-capacity and high-rate compositions were selected for future testing with the program's optimized anodes and electrolytes.

MaxPower, Inc.—Mark Salomon

With a subcontract with Temple University for electrolyte development under the direction of Stephanie Wunder, the effort originally encompassed the development of a two-phase cathode material integrated with Li⁺-conducting polymer electrolytes which were a composite of high molecular weight PEO and either fumed silica nanoparticles or large polyhedral silsesquioxanes (POSS) functionalized with either low molecular weight PEO oligomers or anionically functionalized groups to make a single-ion conductor. Cathode development efforts were deferred after the initial program phase. Partial success was achieved in synthesizing a single-ion conducting polymer, but material scaleup issues prevented this material from being incorporated in demonstration cells.

Several 500 mAh rechargeable pouch cells with a lithium metal/polymer electrolyte/vanadium pentoxide cell configuration were delivered to NASA GRC for electrochemical evaluation. The cell polymer electrolyte consisted of a blend of PEO (600,000 mw) and POSS-(PEO₄)₈ oligomers and lithium salt. Preliminary charge-discharge cycle testing data (initial five cycles) for one of the cells is shown in figure 4. Under the test conditions employed, the cathode developed a specific capacity of 110 mAh/g. The cell was cycled at a low rate for 44 cycles before terminating the test, and a < 0.1% loss in discharge energy per cycle was observed over the length of the test.

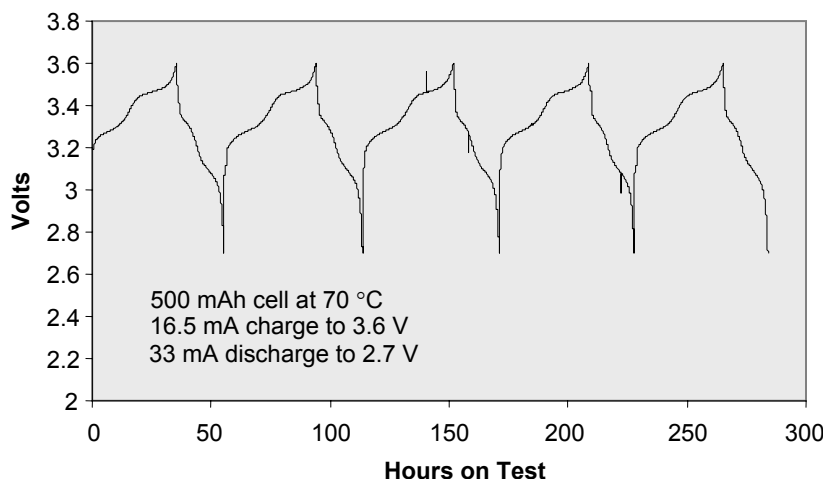


Figure 4.—Cycling data for MaxPower rechargeable polymer electrolyte cell.

Indiana University—Lyudmila Bronstein

The primary focus of this effort was to prepare and investigate polymer electrolytes based upon an organic-inorganic composite (OIC) polymer blend that had been developed at IU. After initial work on hybrid SPEs based on an aluminosilicate structure, an OIC was developed consisting of an amorphous network of a silicate material functionalized with polyethers to provide compatibility with PEO [*J. Mater. Chem.*, **14**, 1812 (2004)]. With an agreement with Sandia National Laboratories, some preliminary electrochemical testing was performed on small lab cells containing composite SPEs and new cathode materials based on TiS_2 microparticles. Very high cell resistance was observed, even at elevated temperatures.

University of Utah—Grant Smith

The objective of the effort was to conduct a joint molecular dynamics (MD) simulations and experimental study of the effect of interfaces on structural and dynamic properties of solid polymer and polymer gel electrolytes. Specifically, MD simulations, conductivity and neutron scattering experiments were utilized and results correlated to understand the effects of nanoparticle fillers in composite PEO-based polymer electrolytes [*Macromolecules*, **36**, 7873 (2003)]. Surface-polymer interactions were found to significantly influence interfacial polymer dynamics. Mechanisms of ion transport in PEO melts were examined over a wide range of compositional variables and temperature, and mechanisms were elucidated [*Macromolecules*, **39**, 1620 (2006)]. Overall, the effort and approach resulted in a better fundamental understanding of ion transport in SPEs and also elucidated the need to address the interfacial properties of electrolytes in addition to bulk properties when designing SPEs for practical batteries. In contrast to many published literature results on the reported advantages of PEO-based composite SPEs, the results from this effort elegantly showed that the addition of nanoparticles does not facilitate ion transport at high temperatures.

Jet Propulsion Laboratory (JPL)—Marshall Smart

Proposed as a multi-year overall program with participation from USC and Hunter College (CUNY), the JPL program would develop and evaluate advanced SPEs via several architectural

approaches – (1) PEO-based composite electrolytes, (2) PEO-based electrolytes with novel architectures (e.g., comb-based systems and star polymer structures), (3) single-ion conducting polyelectrolytes and (4) non-PEO-based polymer electrolyte matrix hosts. Due to reduced funding availability after the first year, this JPL effort had to be formally suspended. During the first year, experimental efforts were focused on composite PEO SPE development activities. Experimental synthesis and evaluation methodologies were established, and a membrane fabrication matrix was employed to examine a host of compositional variables (e.g., particle additive type, concentration and size, PEO molecular weight, O/Li ratio and binary lithium salt type) which led to correlations with critical performance parameters, such as bulk conductivity and stability.

Air Force Research Laboratory (AFRL)—Larry Scanlon

This effort, which had been initiated prior to the PERS Program with Air Force in-house funding, employed a computational chemistry approach to design a totally solid-state material based upon a microstructural “channel” morphology to facilitate lithium-ion conduction in a preferred direction. The ionic transport mechanism is dependent upon the electric field gradient established between the electrodes of an electrochemical cell. Validation of the concept would employ dilithium phthalocyanine (Li_2Pc) as the molecular system (fig. 5).

Phthalocyanine materials were prepared and characterized, ionic conductivity was measured and a small two-electrode electrochemical cell employing the solid-state electrolyte was constructed for initial electrochemical measurements. Due to reduced funding availability after the first year, PERS Program-support had to be suspended for this Air Force effort.

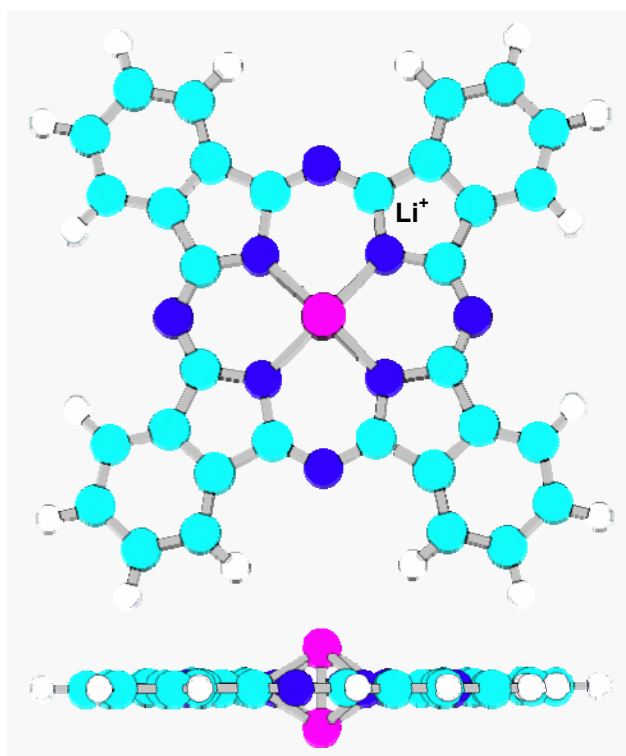


Figure 5.—Dilithium phthalocyanine molecular architecture.

Additional PERS Program Participants

Expertise in the growing field of ionic liquid chemistry realized an effort by *Covalent Associates, Inc.* to explore the concept of a “gelled” ionic liquid-based polymer electrolyte. The substitution of liquid organic solvents in “gelled” electrolyte systems with appropriate ionic liquids of low volatility would enhance safety while maintaining desired ionic conductivity at relatively low temperatures.

Eagle-Picher Technologies, LLC, in collaboration with the University of Oklahoma, undertook some preliminary fundamental research efforts to investigate and assess the use of poly(ethylenimine) (PEI) as a potential alternative to PEO as a polymeric host for advanced composite electrolytes. Strategies to reduce the high degree of crystallinity in linear PEI were developed.

At *EIC Laboratories, Inc.*, several novel concepts were proposed for investigation to address desired low-temperature operation of “nearly dry” polymer electrolytes. Synthesis methodologies were explored to develop single-ion conductors with anchored anionic groups that would form a “channel-like” structure to accommodate a plasticizer or completing agent.

At *InvenTek Corporation*, a program effort was initiated to focus on component development for a safe lithium-based cell chemistry. Work focused on the development of vanadium-based oxide cathodes, surface-modified or alloyed lithium anodes and a PEO-based composite polymer electrolyte containing a flame retardant phosphazene additive for thermal safety in the polymer matrix.

At *LITHCHEM International*, a small research effort was undertaken to develop a new SPE based upon polycarbonate chemistry, rather than state-of-the-art PEO. A number of cyclic and linear oligomers and polymers were synthesized and evaluated with respect to bulk conductivity.

The basis of an approach proposed by *Lithium Power Technologies* was to incorporate a glassy ion-conductor in a PVDF-based polymer matrix to form a composite electrolyte, which could subsequently have its conductivity enhanced by blending with a PEO-based electrolyte. Thin-film fabrication techniques for cell components were also explored.

Research at the *University of Minnesota* focused on employing a novel lithium-ion-conducting salt in a polymer-in-salt morphology. It was found that literature data on the salt was in error. In addition, large polyanionic materials and layered ion-exchanger clays would be explored to form polyelectrolytes.

A PERS-supported effort at the *National Center for Microgravity Research* focused on the utilization of numerical and scaling analyses to assess and model electrochemical cell performance with SPE systems subjected to space and microgravity environments. A major goal was to assess the effects of heat generation on cell performance and assess thermal stresses induced by high recharge rates. The modeling effort would help to understand transport processes and assist in providing a safe battery design rationale prior to costly hardware testing in a microgravity environment.

Two approaches to develop new SPEs were explored at the *Naval Air Warfare Center Weapons Division* at China Lake. One approach was based on crosslinked perfluorosulfonimide/crown ether polymers and blends, while the second approach was to fabricate crystalline channel-containing membranes from crown ether-containing polymers.

At *Northwestern University*, an effort was initiated to utilize their background, skills and resources to develop novel polyelectrolyte materials to address the PERS Program goals. Modeling efforts were to be utilized in the architectural design at the molecular level. A comb polysiloxane polymer-salt complex was synthesized, which had an observed low ionic conductivity.

Physical Sciences, Inc. explored the concept of modifying PEO with pendant anion receptors to prepare a lithium ion-conducting polyelectrolyte, however, synthesis difficulties were encountered.

In collaboration with several subcontractors, *Yardney Technical Products* coupled computational modeling and design methodologies with experimental efforts to synthesize novel materials based on silicon-based and phosphorus-based copolymers. The modification of cathode surfaces was also explored to enhance interfacial properties.

Also in support of the PERS Program, several in-house exploratory R&D efforts were performed within the Power and On-Board Propulsion Technology Division at NASA GRC. One effort was to explore the modification of carbon materials used in composite insertion-type electrodes in lithium-based cell chemistries to enhance interfacial properties and cell performance. In collaboration with Cleveland State University, some initial work was performed to evaluate three polymer electrolyte architectures - crown ether-based, methyl cellulose-based and carbonate-based structures, which were proposed to have molecular-level features that could enhance lithium-ion solvation and transport. Expertise in thin-film deposition and fabrication techniques were also explored for preparing and demonstrating thin-film integrated lithium batteries.

Conclusions

Technically, the PERS Program participants explored to various degrees over the lifetime of the formal program a variety of conceptual approaches for developing and demonstrating performance of a viable advanced solid polymer electrolyte possessing the desired attributes as shown in Table 2, as well as several participants addressing all components of an integrated cell configuration. The electrolytes explored fell into three primary categories – (1) dry, solvent-free systems, which were based on composite PEO (or alternative polymer host morphologies), branched network polymers or novel binary salt systems, (2) single-ion-conducting polyelectrolyte systems and (3) gel-polymer systems. For material samples that were supplied by program participants for evaluation at the NASA GRC facility, the relative bulk ionic conductivities observed for the three categories are compared in figure 6 [W.R. Bennett & R.S. Baldwin, *Assessment of Lithium-based Battery Electrolytes Developed under the NASA PERS Program*, 4th International Energy Conversion Engineering Conference (IECEC), San Diego, CA (2006)]. The best dry SPE evaluated showed a bulk lithium-ion conductivity of $\sim 5 \times 10^{-5}$ S/cm at 25 °C, and gelled electrolytes exhibit an improvement of about one order-of-magnitude. Single-ion conductors have lower bulk conductivity, as there is no mobile anionic charge carrier present in these electrolyte systems. Comparisons of other material and initial electrochemical performance properties for material evaluated at NASA GRC can be found in the reference cited above.

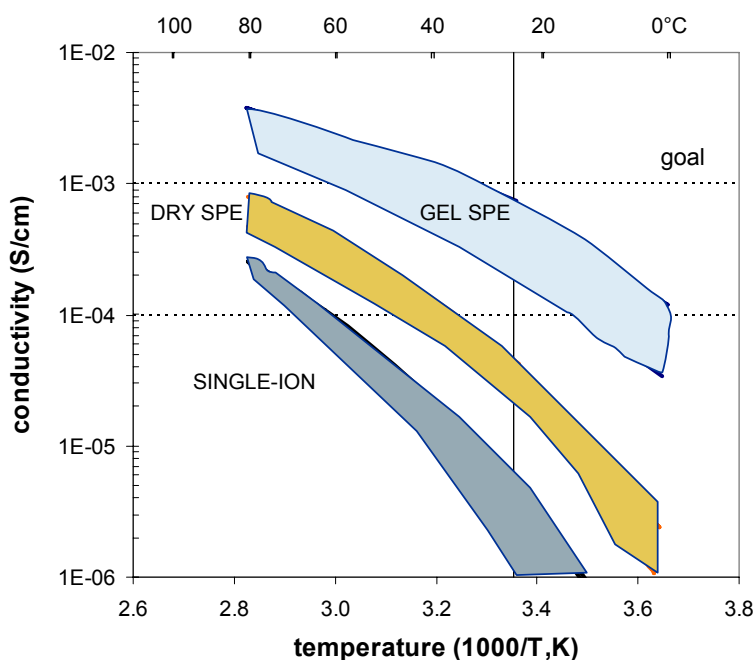


Figure 6.—Bulk ionic conductivity comparisons for PERS SPE material systems.

Programmatically, the NASA PERS Program was very successful, even though the very challenging technical goals for achieving a viable solid polymer electrolyte material or the overall envisioned long-term, program objectives were not met due to funding reductions. In terms of the “return-on-investment” to the government and to the populace, the formal NASA PERS program succeeded in (1) disseminating a large volume of new, fundamental knowledge in polymer and materials science in the public domain, (2) identifying and providing opportunities for new R&D in the national interest and laying a strong foundation for future analogous efforts, (3) creating new and/or strengthening existing industrial, academic and inter-governmental partnerships and (4) enhancing NASA’s technical infrastructure and competencies.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 01-12-2007		2. REPORT TYPE Technical Memorandum		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE The NASA "PERS" Program: Solid Polymer Electrolyte Development for Advanced Lithium-Based Batteries				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Baldwin, Richard, S.; Bennett, William, R.				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER WBS 083229.04.15.01.01.01	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191				8. PERFORMING ORGANIZATION REPORT NUMBER E-16129	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001				10. SPONSORING/MONITORS ACRONYM(S) NASA	
				11. SPONSORING/MONITORING REPORT NUMBER NASA/TM-2007-214965	
12. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified-Unlimited Subject Categories: 27 and 44 Available electronically at http://gltrs.grc.nasa.gov This publication is available from the NASA Center for AeroSpace Information, 301-621-0390					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT In fiscal year 2000, The National Aeronautics and Space Administration (NASA) and the Air Force Research Laboratory (AFRL) established a collaborative effort to support the development of polymer-based, lithium-based cell chemistries and battery technologies to address the next generation of aerospace applications and mission needs. The ultimate objective of this development program, which was referred to as the Polymer Energy Rechargeable System (PERS), was to establish a world-class technology capability and U.S. leadership in polymer-based battery technology for aerospace applications. Programmatically, the PERS initiative exploited both interagency collaborations to address common technology and engineering issues and the active participation of academia and private industry. The initial program phases focused on R&D activities to address the critical technical issues and challenges at the cell level. Out of a total of 38 proposals received in response to a NASA Research Announcement (NRA) solicitation, 18 proposals (13 contracts and 5 grants) were selected for initial award to address these technical challenges. Brief summaries of technical approaches, results and accomplishments of the PERS Program development efforts are presented. With Agency support provided through FY 2004, the PERS Program efforts were concluded in 2005, as internal reorganizations and funding cuts resulted in shifting programmatic priorities within NASA. Technically, the PERS Program participants explored, to various degrees over the lifetime of the formal program, a variety of conceptual approaches for developing and demonstrating performance of a viable advanced solid polymer electrolyte possessing the desired attributes, as well as several participants addressing all components of an integrated cell configuration. Programmatically, the NASA PERS Program was very successful, even though the very challenging technical goals for achieving a viable solid polymer electrolyte material or the overall envisioned long-term, program objectives were not met due to funding reductions. The NASA PERS Program provided research opportunities and generated and disseminated a wealth of new scientific knowledge and technical competencies within the polymer electrolyte area.					
15. SUBJECT TERMS Electrochemistry; Energy storage; Lithium battery; Polymer					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 21	19a. NAME OF RESPONSIBLE PERSON STI Help Desk (email: help@sti.nasa.gov)
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (include area code) 301-621-0390

